

CD221. LECTURE 13. THE LANGMUIR ISOTHERM. FLUCTUATIONS.

- The Ideal Gas within the Grand Canonical Formalism

The equation of state of an ideal gas can be derived from the grand canonical formalism too, as we'll now show. The reason for doing this is to reinforce the idea that it doesn't matter which partition function you use to derive the thermodynamic properties of a system – they're all effectively equivalent (although one partition function might arrive at the answer faster than another.) This is not too surprising, since the different partition functions simply lead to different thermodynamic potentials, and these potentials are equivalent in terms of the thermodynamic information they contain.

The starting point for the calculation of the ideal gas the equation of state is the grand partition function Ξ , defined as

$$\Xi = \sum_{\alpha} e^{-\beta(U_{\alpha} - \mu N_{\alpha})} \quad (1)$$

If we recall that a sum over states can be written equivalently as a sum over *levels*, where a level in the present case refers to a macrostate with definite values of *both* U and N , we can write Eq. (1) as

$$\Xi = \sum_U \sum_{N=0}^{\infty} \Omega(U, N, V) e^{-\beta U + \beta \mu N} \quad (2)$$

where as usual $\Omega(U, N, V)$ is the multiplicity (microcanonical partition function) of the macrostate with energy U and number of particles N . It's also useful here to note that (i) the probability $p_{U,N}$ that the system occupies the *macrostate* with U and N , is

$$p_{U,N} = \frac{1}{\Xi} \Omega(U, N, V) e^{-\beta U + \beta \mu N} \quad (3)$$

and that (ii) the probability p_N that it occupies the macrostate with just N , irrespective of what energy it has, is

$$p_N = \frac{1}{\Xi} \sum_U \Omega(U, N, V) e^{-\beta U + \beta \mu N} \quad (4)$$

If the sum in Eq. (2) is now rearranged to

$$\Xi = \sum_{N=0}^{\infty} \left(\sum_U \Omega(U, N, V) e^{-\beta U} \right) e^{\beta \mu N} \quad (5)$$

we can recognize that the sum in parentheses is just the sum-over-levels representation of the canonical partition function Q . So Eqs. (2) and (4) can be rewritten as

$$\Xi = \sum_{N=0}^{\infty} Q(T, V, N) e^{\beta \mu N} \quad (6a)$$

and

$$p_N = \frac{1}{\Xi} Q(T, V, N) e^{\beta \mu N} \quad (6b)$$

We already know what $Q(T, V, N)$ is for the ideal gas; it is

$$Q(T, V, N) = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} V^N \quad (7)$$

If we now substitute Eq. (7) into Eq. (6a), we arrive at

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V e^{\beta \mu} \right]^N \quad (8)$$

which we can write in the form

$$\Xi = \sum_{N=0}^{\infty} \frac{\xi^N}{N!} \quad (9)$$

by introducing the definition

$$\xi \equiv \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V e^{\beta \mu} . \quad (10)$$

The sum in Eq. (9) is the series representation of the exponential function, so Ξ can be obtained in closed form as

$$\Xi = e^{\xi} \quad (11)$$

and since $\Psi = -k_B T \ln \Xi$, we find that

$$\Psi = -k_B T \xi . \quad (12)$$

This result looks quite suggestive, and it becomes even more suggestive when we recall two facts: one, that by definition of the Legendre transform, $\Psi = U - TS - \mu N$, and two, that by the Euler relation, $U = TS - PV + \mu N$. Together, these equations tell you that $\Psi = -PV$, and so

$$PV = k_B T \xi \quad (13)$$

This is almost the ideal gas equation, except that there's no N on the right hand side of the equation – what appears there instead is the chemical potential μ . So to recover the ideal gas equation in its familiar form, it's necessary to somehow eliminate μ in favour of N . To do this, we consider the two expressions we've derived for Ξ in Eqs. (9) and (11). If we differentiate Eq. (9) with respect to ξ , we get

$$\frac{\partial \Xi}{\partial \xi} = \sum_{N=0}^{\infty} N \frac{\xi^{N-1}}{N!} = \frac{1}{\xi} \sum_{N=0}^{\infty} N \frac{\xi^N}{N!} \quad (14)$$

which can be rearranged to

$$\xi \frac{\partial \Xi}{\partial \xi} = \sum_{N=0}^{\infty} N \frac{\xi^N}{N!} \quad (15)$$

If we now similarly differentiate Eq. (11) with respect to ξ , we see that

$$\frac{\partial \Xi}{\partial \xi} = e^{\xi} = \Xi \quad (16)$$

Putting this result back in Eq. (15), we find that

$$\xi = \frac{1}{\Xi} \sum_{N=0}^{\infty} N \frac{\xi^N}{N!} \quad (17)$$

On the right hand side of this equation, we can now re-introduce the original definition of ξ in terms of the canonical partition function Q . Referring to Eqs. (7) and (10), we see that this leads to the result

$$\xi^N = N! Q(T, V, N) e^{\beta \mu N} \quad (18)$$

Substituting this result into Eq. (17) and recalling the definition of p_N in Eq. (6b), we finally arrive at

$$\xi = \sum_{N=0}^{\infty} N p_N = \bar{N} \quad (19)$$

which, after substitution into Eq. (13), then leads to $PV = \bar{N}k_B T$, which is our old friend the ideal gas equation. It took some work to get to this point, but in the end we've found that the grand canonical formalism predicts exactly the same mechanical equation of state as the earlier two formalisms.

- Another Application of the Grand Canonical Formalism: The Langmuir Isotherm

There are certain problems for which the grand canonical formalism is naturally suited. The adsorption of gas molecules onto a solid surface is the classic example. Consider a solid (Pt, say), in some volume V and at some temperature T in equilibrium with a gas (H_2 , for instance) at some pressure P . Assume that the solid has M lattice sites, and that each site can reversibly adsorb at most one molecule of the gas at any one instant of time. The system is shown schematically below.

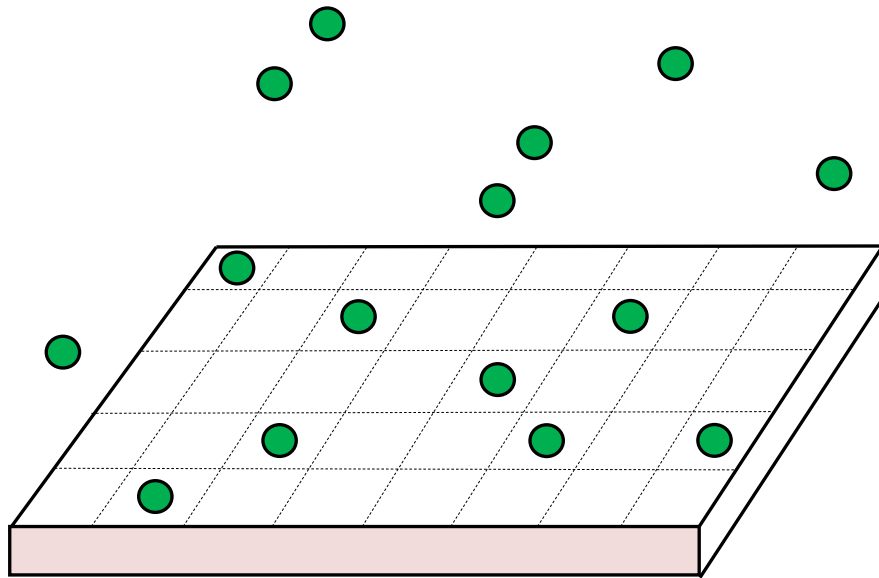


FIGURE 1

If adsorption is energetically favorable, such that in the adsorbed state the energy of the gas molecule is $-\varepsilon$, with $\varepsilon > 0$, a question of immediate interest is: what fraction of the solid sites are occupied by the gas?

In addressing this question, it's important to note that the system is the solid and *adsorbed* gas. The molecules of gas surrounding the solid should be thought of as a particle reservoir of fixed chemical potential μ . The number of gas molecules on the surface is clearly not constant but fluctuates, and at equilibrium, under the given

conditions of T and μ , it has some average value \bar{N} . If we can determine the grand canonical partition function of the system, Ξ , we can find \bar{N} from the formula

$$\bar{N} = - \left(\frac{\partial \Psi}{\partial \mu} \right)_{T,V} \quad (20)$$

For the present problem, it proves convenient to calculate Ψ from the sum-over-levels representation of Ξ :

$$\Xi = \sum_{\text{levels}} \Omega(U, V, N) e^{-\beta(U - \mu N)} \quad (21)$$

Since the energy from the binding at a single site is $-\varepsilon$, the adsorption of N molecules onto the surface leads to a total energy of $-N\varepsilon$. So the possible energy levels of the system are just the different energies that are obtained for different values of N . Furthermore, for every given energy level (i.e., for every macrostate of N adsorbed molecules) there are Ω different ways of arranging these molecules on the M sites. Taking the molecules (or the lattice sites, to be more precise) to be distinguishable, we see that Ω must be

$$\Omega = \frac{M!}{N!(M-N)!} \quad (22)$$

Since every energy level corresponds to some value of N , and since N cannot be greater than M , the sum in Eq. (21), after introducing Eq. (22), actually reduces to

$$\begin{aligned} \Xi &= \sum_{N=0}^M \frac{M!}{N!(M-N)!} e^{\beta(N\varepsilon + \mu N)} \\ &= \sum_{N=0}^M \frac{M!}{N!(M-N)!} \left(e^{\beta(\varepsilon + \mu)} \right)^N \end{aligned} \quad (23)$$

The above sum should be recognized as a binomial expansion. That is,

$$\Xi = \left[1 + e^{\beta(\varepsilon + \mu)} \right]^M \quad (24)$$

Now that we've calculated the partition function exactly, we're in a position to determine all of the system's thermodynamic properties. In particular, using Eq. (20), we find that the average number of gas molecules on the surface is given by

$$\bar{N} = \left(\frac{\partial}{\partial \mu} k_B T \ln \left[1 + e^{\beta(\varepsilon + \mu)} \right]^M \right)_{T,V}$$

$$\begin{aligned}
&= M k_B T \frac{e^{\beta(\varepsilon+\mu)}}{1+e^{\beta(\varepsilon+\mu)}} \beta \\
&= M \frac{e^{\beta(\varepsilon+\mu)}}{1+e^{\beta(\varepsilon+\mu)}}
\end{aligned} \tag{25}$$

The fractional occupancy of the surface is just $\bar{N}/M \equiv \theta$, so from Eq. (25), we have

$$\theta = \frac{1}{1+e^{-\beta(\varepsilon+\mu)}} \tag{26}$$

This is essentially the answer we were looking for, except that it is preferable to express it in terms of the pressure P rather than the chemical potential μ because in a laboratory setting it is the former that is experimentally controlled. Rewriting Eq. (26) in terms of P is easily done if we assume that the gas is ideal. For an ideal gas we know that the canonical partition function Q is

$$Q = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} V^N \tag{27}$$

and so the Helmholtz free energy F is given by

$$F = -k_B T \left[-\ln N! + \frac{3N}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) + N \ln V \right] \tag{28}$$

Recalling that $dF = -SdT - PdV + \mu dN$, and hence that $\mu = (\partial F / \partial N)_{T,V}$, we see from Eq. (28), after using Stirling's approximation, that

$$\mu = -k_B T \left[-\ln N + \frac{3}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) + \ln V \right] \tag{29}$$

After rearranging and exponentiating Eq. (29), we obtain

$$e^{-\beta\mu} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{V}{N} \tag{30}$$

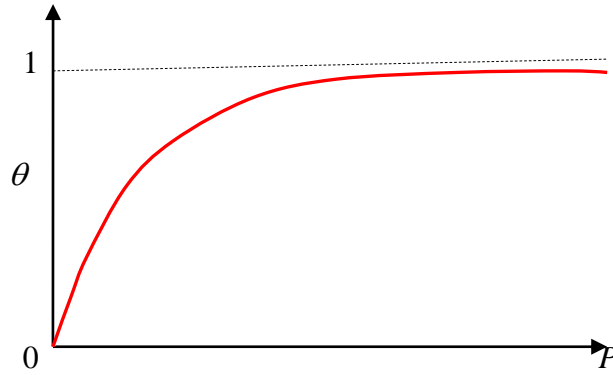
If the ideal gas law $PV = Nk_B T$ is now used in Eq. (30) to eliminate N , we finally arrive at

$$e^{-\beta\mu} = \frac{k_B T}{P} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \quad (31)$$

Defining a reference pressure P_0 as $P_0 = e^{-\beta\epsilon} k_B T (2\pi m k_B T / h^2)^{3/2}$, and substituting this definition along with Eq. (31) into Eq. (26), we obtain the famous Langmuir adsorption isotherm:

$$\theta = \frac{P}{P_0 + P} \quad (32)$$

A plot of θ vs P at constant T yields a familiar saturation curve, as depicted in the figure below



• Averages and Fluctuations

We've seen that when a system is maintained at a constant value of some intensive variable F_0 (by contact with a suitable reservoir), the value of its conjugate extensive variable X_0 is not constant but fluctuates in time. We've also seen that over long periods of time, this fluctuating variable is *averaged* to some time-independent value \bar{X}_0 . We've formally defined this average as

$$\bar{X}_0 = \sum_{\alpha} p_{\alpha} X_{0\alpha} \quad (33)$$

where p_{α} is the probability that the system is in some state α , and $X_{0\alpha}$ is the value of X_0 in α . The same considerations hold when other intensive variables in the system, say, F_1, F_2, \dots, F_s , are kept constant; now there are also fluctuations in the corresponding

set of conjugate extensive variables, X_1, X_2, \dots, X_s . These variables too are averaged to the time-independent $\bar{X}_1, \bar{X}_2, \dots, \bar{X}_s$, where, in general

$$\bar{X}_i = \sum_{\alpha} p_{\alpha} X_{i\alpha}, \quad i = 1, 2, \dots, s \quad (34)$$

A question of immediate interest is the following: how large – *on average* – can we expect deviations from such average values to be? One widely used measure of the size of a deviation (or fluctuation), is the following:

$$\sigma_{X_i}^2 = \overline{(X_{i\alpha} - \bar{X}_i)^2} \quad (35)$$

which will be recognized as the definition of a quantity called the variance. The square root of the variance is the standard deviation, and it is one of two numbers that we typically report when discussing, say, class performance on a CD221 homework assignment (the other number being, of course, the average.) The variance and standard deviation say something about how widely spread a set of values are about their average.

The overbar in Eq. (35) is interpreted according to the definition in (34). In other words,

$$\sigma_{X_i}^2 = \sum_{\alpha} p_{\alpha} (X_{i\alpha} - \bar{X}_i)^2, \quad (36)$$

or, expanding out the term in parentheses,

$$\begin{aligned} \sigma_{X_i}^2 &= \sum_{\alpha} p_{\alpha} (X_{i\alpha}^2 - 2X_{i\alpha}\bar{X}_i + \bar{X}_i^2) \\ &= \sum_{\alpha} p_{\alpha} X_{i\alpha}^2 - 2\bar{X}_i \sum_{\alpha} p_{\alpha} X_{i\alpha} + \bar{X}_i^2 \sum_{\alpha} p_{\alpha} \\ &= \overline{X_i^2} - 2\bar{X}_i^2 + \bar{X}_i^2 \\ &= \overline{X_i^2} - \bar{X}_i^2 \end{aligned} \quad (37)$$

Let's now see what the application of this formula to some specific examples can tell us. So consider first a system at constant T (at fixed V and N .) The variable that fluctuates as the result of the constancy of T is the energy U . We've shown that the probability p_{α} that system is in state α is $e^{-\beta U_{\alpha}} / Q$. With this expression, and identifying X_i with U , the average $\overline{X_i^2}$ in Eq. (37) becomes

$$\begin{aligned}
\overline{U^2} &= \sum_{\alpha} \frac{e^{-\beta U_{\alpha}}}{Q} U_{\alpha}^2 \\
&= \frac{1}{Q} \frac{\partial^2}{\partial \beta^2} \sum_{\alpha} e^{-\beta U_{\alpha}} \\
&= \frac{1}{Q} \frac{\partial^2 Q}{\partial \beta^2}
\end{aligned} \tag{38}$$

Similarly,

$$\begin{aligned}
\overline{U^2} &= \left(\sum_{\alpha} \frac{e^{-\beta U_{\alpha}}}{Q} U_{\alpha} \right)^2 \\
&= \left(-\frac{1}{Q} \frac{\partial}{\partial \beta} \sum_{\alpha} e^{-\beta U_{\alpha}} \right)^2 \\
&= \left(-\frac{1}{Q} \frac{\partial Q}{\partial \beta} \right)^2
\end{aligned} \tag{39}$$

Substituting Eqs. (38) and (39) into Eq. (37), we obtain the following expression for the variance:

$$\sigma_U^2 = \frac{1}{Q} \frac{\partial^2 Q}{\partial \beta^2} - \frac{1}{Q^2} \left(\frac{\partial Q}{\partial \beta} \right)^2 \tag{40}$$

which simplifies to

$$\sigma_U^2 = \frac{\partial^2 \ln Q}{\partial \beta^2} \tag{41}$$

But $\ln Q = -\beta F$ (F being the Helmholtz potential), and when this relation is substituted into Eq. (41), we get

$$\begin{aligned}
\sigma_U^2 &= -\frac{\partial^2 (\beta F)}{\partial \beta^2} \\
&= -\frac{\partial}{\partial \beta} \left(F + \beta \frac{\partial F}{\partial \beta} \right)
\end{aligned}$$

$$= -2 \frac{\partial F}{\partial \beta} - \beta \frac{\partial^2 F}{\partial \beta^2} \quad (42)$$

Although not indicated explicitly, the partial derivatives in these expressions are taken at constant V and N , so $\partial F / \partial \beta = k_B T^2 S$ and $\partial^2 F / \partial \beta^2 = (1/k_B)(-2\beta^{-3}S + \beta^{-2}\partial S / \partial \beta)$. Hence,

$$\sigma_U^2 = -T \frac{\partial S}{\partial \beta} = k_B T^2 C_V \quad (43)$$

where C_V is the constant volume heat capacity. The standard deviation in energy fluctuations is just the square root of σ_U^2 , and therefore

$$\sigma_U = \sqrt{k_B T^2 C_V} \quad (44)$$

To get a better feel for what this relation means, consider an ideal gas; for this system C_V is on the order of Nk_B , which means that $\sigma_U \sim O(N^{1/2})$. Fluctuations around \bar{U} therefore tend to become larger and larger as the system increases in size. But \bar{U} itself increases with system size, and it does so much faster than σ_U . For an ideal gas, for instance, \bar{U} is on the order of $Nk_B T$, i.e., $\bar{U} \sim O(N)$, so it is really the size of the fluctuations *in relation to* the mean that provides a better measure of how significant the fluctuations are. Defining the *relative* size of a fluctuation as σ_U / \bar{U} , we see that for the ideal gas (and in general for other systems as well),

$$\frac{\sigma_U}{\bar{U}} \sim O(N^{-1/2}) \quad (45)$$

In a typical macroscopic system at constant T , therefore, the relative deviations from the mean are minuscule, and the likelihood (probability) of observing the system with an energy that departs significantly from this value is negligible.

We can actually quantify this probability. But to do so, we need to derive an expression for *distribution* of possible U values, a problem we'll take up in the next section.